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XAFS SPECTRA AND THE OXIDATION STATE OF NICKEL IN SOME OF ITS OXYCOMPOUNDS

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ABSTRACT

XANES spectra of nickel K-edge and X-ray diffraction patterns of several nickel oxycompounds were measured. The shift in energy of the Ni K-absorption edge towards higher values correlates well with the increase in the oxidation state of nickel from +2 to +4 in the compounds studied. The inflection point energy of the Ni pre-edge structure shifts approximately 1 eV per unit change in valency. Our results provide evidence which supports the assignment that the valency of Ni in β-NiOOH is +3; $Ni_3O_2(OH)_4$ and commercial "nickel peroxide" (NiO_2) likewise contain trivalent nickel. The edge shift for quadrivalent nickel in $KNiIO_6$ is reported for the first time.

INTRODUCTION

The structure of the higher oxide forms of nickel (where Ni has a valency greater than + 2) is of great interest from the standpoint of developing advanced nickel batteries for consumer applications and for electric vehicle propulsion. In spite of the considerable research work that has been published, there is still much uncertainty and confusion as to the stoichiometry and structure of the various oxides (hydroxides) that are formed during the charging (and discharging) of the nickel electrode.[1] The oxidation states of Ni in these compounds are of particular interest and need clarification. The difficulty stems in part from the highly disordered or amorphous nature of the phases formed which makes structural determination by X-ray diffraction difficult. X-ray absorption fine structure (XAFS) spectroscopy which consists of measuring the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) is an excellent technique for the characterization of such materials with no long range order.[2-5] Preliminary to using the technique for "in-situ" structural determinations in an electrochemical cell, we have used XAFS spectroscopy to study a number of nickel compounds namely metallic Ni, NiO, β-NiOOH, $Ni_3O_2(OH)_4$, NiO_2 and $KNiIO_6$ for subsequent use as references in the identification of electrochemically formed phases. We report initial XAFS results that give an indication of the valency of nickel in some compounds of interest in battery work. Results from quantitative analysis of the EXAFS data will be presented in another publication.

EXPERIMENTAL

The compounds studied were prepared by chemical synthesis following procedures established in the literature; others were purchased from commercial suppliers. The β-NiOOH was prepared by bromine oxidation of $Ni(NO_3)_2$ solution at low temperatures (< 25 °C) following the procedure of Glemser.[6] The $Ni_3O_2(OH)_4$ was obtained by bromine oxidation of $Ni(NO_3)_2$ in an aqueous alkaline solution at 50 °C. The black precipitate was washed, filtered, and dried in a vacuum desiccator.[6] The $KNiIO_6$ was synthesized following the procedure of Murthy[7] for the peroxydisulfate oxidation of a solution of $NiSO_4$ + KIO_4. The nickel oxide (NiO) and "nickel peroxide" (NiO_2) were purchased from Aldrich Chemical Co. (Milwaukee, WI). All samples were examined by powder X-ray diffraction (XRD). The X-ray absorption fine structure spectra were measured at beamline X-11A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, in Upton, NY. Data were collected with a variable exit double-crystal monochromator using two flat Si(111) crystals. Room temperature spectra of the Ni K-edge (8333 eV) were measured in transmission mode with the storage ring operating at 2.52 GeV electron energy and currents in the range of 110-220 mA. The spectrum of a 6 μm thick Ni foil was measured simultaneously with each sample for use as a reference in calibrating the energy scale.

RESULTS AND DISCUSSION

Figure 1a shows the XANES spectra at room temperature of NiO, β-NiOOH

$Ni_3O_2(OH)_4$, NiO_2 and $KNiIO_6$ along with Ni foil used as reference. The pre-edge region from 8323 to 8335 eV, for the oxides, has been expanded to clearly display the contribution due to the transition from the 1s core level to bound unoccupied d-states near the Fermi level and is shown in Figure 1b. For insulators such as these oxides, bound excited states (also referred to as core excitons) appear below the continuum threshold. In insulators, the core hole is only partially screened in contrast to metals where screening is normally complete. Because of the photoelectron-core hole interaction in oxides, the pre-edge structure can be described by molecular orbitals of the cluster formed by the absorbing and backscattering atoms. In addition, due to the different types of backscattering atoms in metallic Ni and the oxides, it is inappropriate to directly compare the spectrum of metallic Ni to the spectra of the oxides in the pre-edge region. The weak intensity associated with this transition is due to the fact that this transition is forbidden by dipole selection rules. It is allowed by quadrupole selection rules or as a result of hybridization between unoccupied states with p and d characters. The nature of d-states near the Fermi level strongly depends on the chemical environment and their signatures in the XANES is expected to vary with changes in Ni valency. The Ni K-edge energies are listed in Table I. X-ray diffraction patterns of the materials are shown in Figure 2. The XRD pattern indicated that both the NiO and $KNiIO_6$ were fairly crystalline with sharp lines while the others showed broad bands indicative of highly disordered or amorphous materials. An examination of the data presented in Figure 1a leads to some interesting observations. As expected, the Ni K-edge shifts to higher energies as the

oxidation state increases from Ni^{o} (metallic Ni), to Ni^{+2} (NiO) and Ni^{+4} ($KNiIO_6$). The latter is among the few compounds where Ni has been fairly well established to be in the quadrivalent state[8] and was chosen here as a reference because of its stability and ease of preparation. We believe that this is the first published XANES spectrum of a quadrivalent Ni compound. The observed shifts suggest that in β-NiOOH, the Ni is in the + 3 state. The compound formulated as Ni_3O_2 $(OH)_4$ shows a shift identical to that of β-NiOOH, although a slight difference is observed in their XRD patterns (Figure 2). In fact, the XANES spectra for both β-NiOOH and $Ni_3O_2(OH)_4$ are essentially the same and, hence, indistinguishable from each other. The formulation that $Ni_3O_2(OH)_4$ is a hydroxide remains highly questionable in view of the absence of OH stretching vibrations in the Raman spectra.[9] We suggest that this stoichiometric formula is a misnomer and its further use should be discouraged. The EXAFS spectra and their corresponding Fourier transforms for β-NiOOH and $Ni_3O_2(OH)_4$ are also very similar. The inflection point energy at the onset of the 1s to 3d transition (Figure 1b) also shifts to higher energy with increase in valency of Ni from Ni^{+2} (NiO) to Ni^{4+} ($KNiIO_6$) with those of β-NiOOH and $Ni_3O_2(OH)_4$ being intermediate between Ni^{+2} and Ni^{+4} indicating a Ni valency of +3 for both compounds. We find a linear relationship between the edge energy and the Ni valency assuming a Ni valency of +3 for both β-NiOOH and $Ni_3O_2(OH)_4$. Note that both NiO and $KNiIO_6$ display a sharp pre-edge peak characteristic of the ordered Ni octahedral coordination (i.e., in both compounds the local structure can be described by an NiO_6 cluster with a single NiO distance) in these compounds. The β-NiOOH and $Ni_3O_2(OH)_4$, on the other hand, each display a

broad pre-edge peak which may be due to a Ni distorted octahedral coordination (i.e., in both compounds the local structure can be described by an NiO_6 cluster with two NiO distances) as revealed from analysis of EXAFS data. The "nickel peroxide" (NiO_2) purchased from Aldrich Chemical Co. does not have Ni in the + 4 state but is most probably a Ni^{+3} compound. The XANES of NiO_2 resemble more closely those of β-NiOOH and $Ni_3O_2(OH)_4$ rather than that of $KNiIO_6$ in terms of edge energy and peak shape. The EXAFS spectrum of NiO_2 is also similar to those of β-NiOOH and $Ni_3O_2(OH)_4$. The Raman spectrum of this material shows two bands at 470 and 550 cm^{-1} similar to β-NiOOH and other higher oxide forms which we have studied.[10] In fact the XRD pattern for NiO_2 (Figure 2) is nearly identical to that of the β-NiOOH except for the sharp lines superimposed on the broad bands. These sharp lines which correspond to values of "d" spacings equal to 3.246, 2.817, 1.991, 1.551 and 1.407 Å are due to NaCl which presumably was not removed during the synthesis of the material. The presence of NaCl, however, does not interfere in the XANES measurement.

We have also synthesized γ-NiOOH and measured its X-ray absorption spectrum. However, the material we obtained following the procedure of Bartl et al.[11] appears to always consist of a mixed phase and yielded a K-edge shift similar to β-NiOOH. Attempts are being made to prepare purer samples and further characterize these by X-ray absorption spectroscopy.

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TABLE I. Ni K-edge Energy in Various Compounds*

Compound	Ni K-edge Energy[1]	Ni K-edge Energy[2]
Ni	8336.9	N/A
NiO	8338.9	8328.9
β-NiOOH	8340.8	8329.6
$Ni_3O_2(OH)_4$	8340.8	8329.6
NiO_2	8340.2	8329.6
$KNiIO_6$	8343.0	8330.6

* Energies are accurate to within ± 0.2 eV

[1] Ni K-edge energy measured as the energy at which the normalized absorption (μx) is equal to 0.5 (i.e., the absorption at half-height of the edge step).

[2] Ni K-edge energy measured as the energy of the inflection point at the onset of the 1s to 3d transition. This procedure is not applicable (N/A) to Ni metal data due to the extremely low transition probability for quadrupole transitions and the lack of hybridization between p- and d-states near the Fermi level for metallic Ni.

FIGURES CAPTION

Figure 1a XANES of Ni K-edge in some of its compounds: Ni foil, NiO, β-NiOOH, $Ni_3O_2(OH)_4$, NiO_2, and $KNiIO_6$. Note that both β-NiOOH and $Ni_3O_2(OH)_4$ display essentially identical spectra.

Figure 1b Pre-edge structure of Ni K-edge displaying the 1s to 3d transition for some nickel compounds: NiO, β-NiOOH, $Ni_3O_2(OH)_4$, NiO_2, and $KNiIO_6$. Note that both β-NiOOH and $Ni_3O_2(OH)_4$ display essentially identical spectra.

Figure 2 X-ray powder diffraction patterns for some nickel compounds: a) NiO, b) β-NiOOH, c) $Ni_3O_2(OH)_4$, d) NiO_2, and e) $KNiIO_6$.

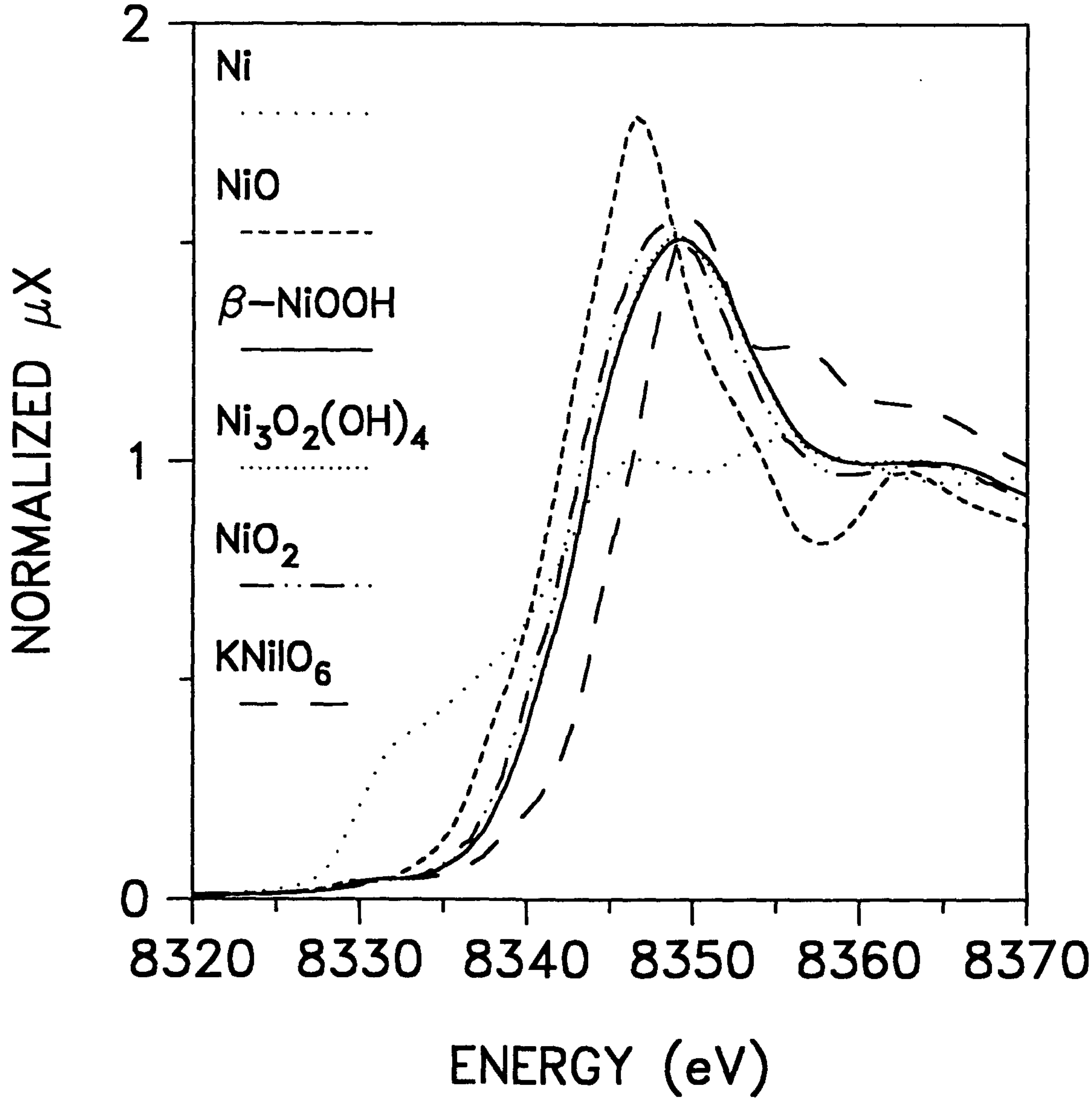
2
1
0
Ni
NiO
β−NiOOH
Ni3O2(OH)4
NiO2
KNiIO6
NORMALIZED μX
8320
8330
8340
8350
8360
8370
ENERGY (eV)

Figure 1a

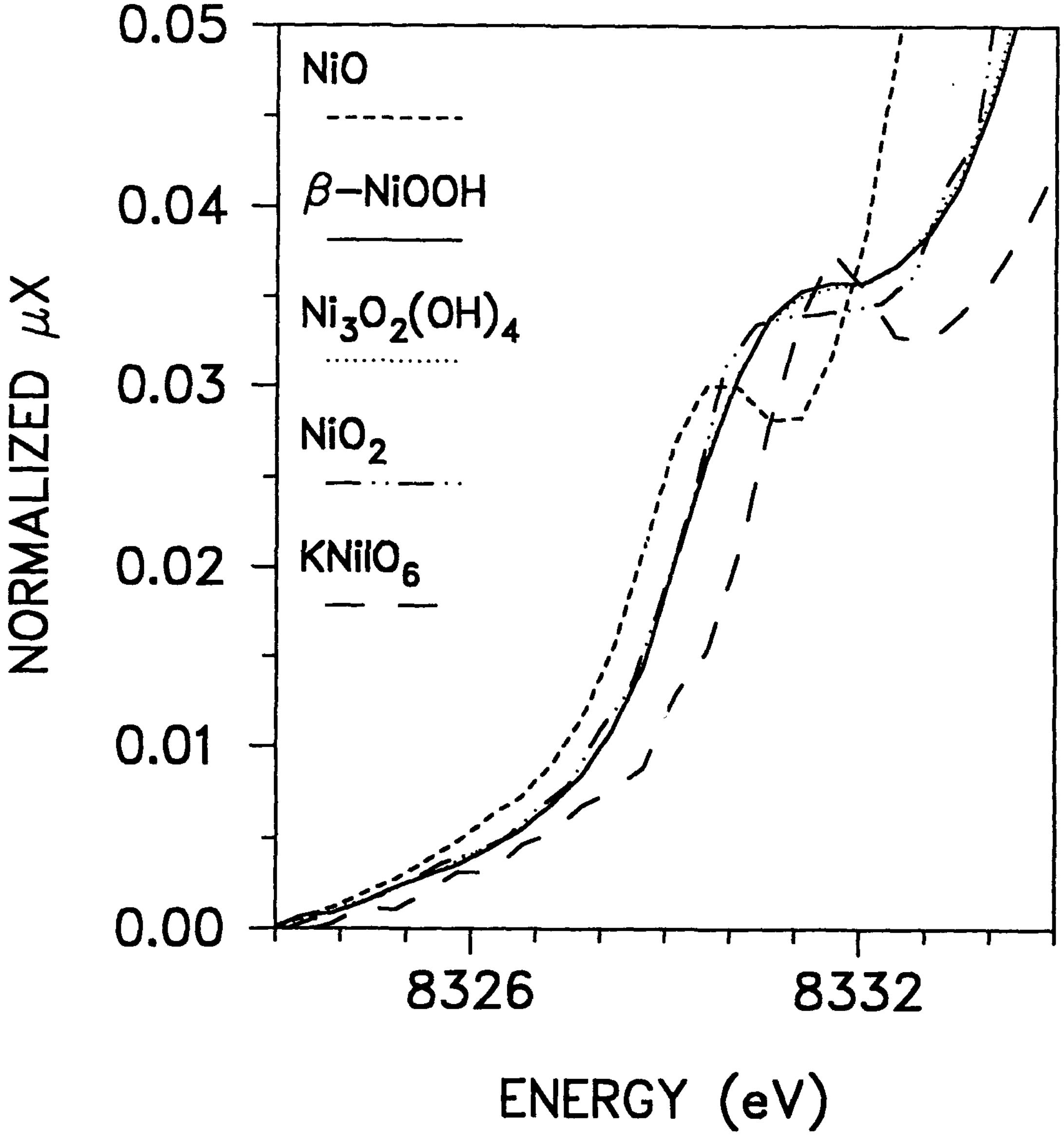
NORMALIZED μX
0.05
0.04
0.03
0.02
0.01
0.00
NiO
β−NiOOH
Ni3O2(OH)4
NiO2
KNiIO6
8326
8332
ENERGY (eV)

Figure 1b

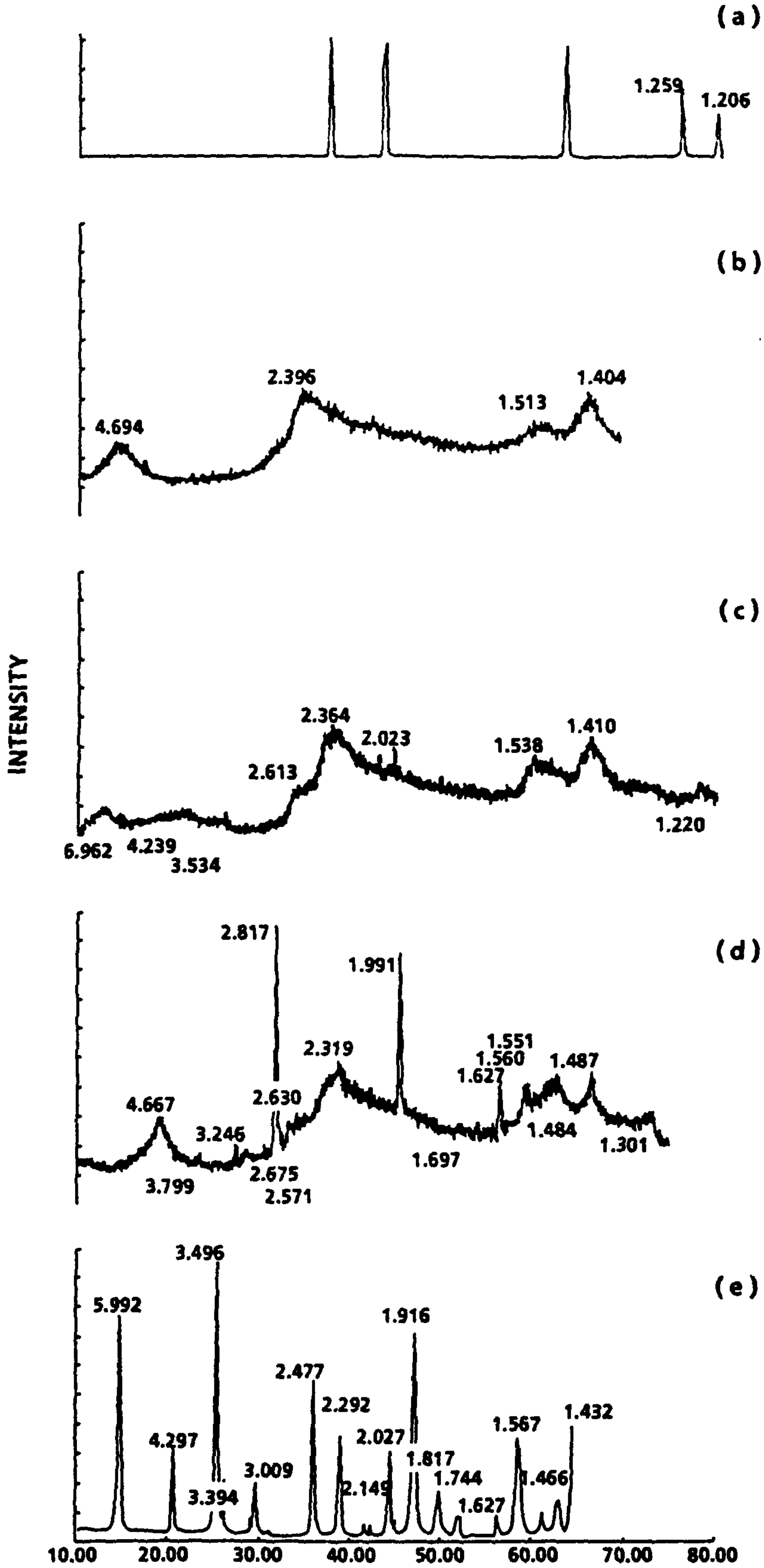
(a)
1.259
1.206
(b)
4.694
2.396
1.513
1.404
(c)
INTENSITY
2.364
2.023
2.613
1.538
1.410
6.962
4.239
3.534
1.220
(d)
2.817
1.991
2.319
1.551
1.560
1.627
1.487
4.667
2.630
3.246
1.484
1.301
3.799
2.675
2.571
1.697
(e)
3.496
5.992
1.916
2.477
2.292
4.297
2.027
1.567
1.432
3.009
1.817
3.394
2.149
1.744
1.466
1.627
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00

Figure 2